



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>7</sup> :  C07C 1/04, 27/00		A1	(11) International Publication Number: <b>WO 00/63141</b>  (43) International Publication Date: 26 October 2000 (26.10.00)		
(21) International Application Number: PCT/US00/10911			(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).		
(22) International Filing Date: 21 April 2000 (21.04.00)					
(30) Priority Data: 09/295,989 21 April 1999 (21.04.99) US					
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(54) Title: MULTIPLE REACTOR SYSTEM AND METHOD FOR FISCHER-TROPSCH SYNTHESIS

## (57) Abstract

A Fischer-Tropsch process is provided for synthesizing hydrocarbons, involving multiple Fischer-Tropsch reactor stages (110) arranged in series, and characterized by very low carbon monoxide conversion per Fischer-Tropsch reactor stage (110) and intermediate removal of water between reactor stages (110). In one embodiment, the system utilizes an iron-based catalyst and balances the molar H<sub>2</sub>/CO feed ratio in the synthesis gas (108) with the overall H<sub>2</sub>/CO consumption ratio across all of the Fischer-Tropsch reactor stages (110). In a preferred embodiment, carbon dioxide is recycled from the last in series of the Fischer-Tropsch reactor stages (110) to the synthesis gas generator (106). The system may advantageously utilize a gaseous hydrocarbon feed (102), such as obtained from natural gas, as feed for producing the synthesis gas (108).

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**MULTIPLE REACTOR SYSTEM AND METHOD  
FOR FISCHER-TROPSCH SYNTHESIS**

**FIELD OF THE INVENTION**

5 The present invention relates in general to Fischer-Tropsch synthesis of hydrocarbons from synthesis gas and, in particular, to Fischer-Tropsch synthesis involving a plurality of staged Fischer-Tropsch reactors which may be operated in a manner that is especially advantageous when using a gaseous hydrocarbon feed, such as natural gas, that tends to produce hydrogen-rich synthesis gas.

**BACKGROUND OF THE INVENTION**

10 Fischer-Tropsch processing is a well known technique for synthesizing hydrocarbon products. In general, Fischer-Tropsch synthesis processes involves converting a synthesis gas including hydrogen and carbon monoxide to hydrocarbon products in the presence of a Fischer-Tropsch catalyst. The most commonly used Fischer-Tropsch catalysts are iron-based and cobalt-based.

15 A Fischer-Tropsch process is generally thought to involve a complex combination of reactions. Some important reactions include the following:

- I.  $2 H_2 + CO \rightarrow -CH_2- + H_2O$
- II.  $H_2O + 3CO \rightarrow -CH_2- + 2CO_2$
- III.  $H_2O + CO \rightarrow CO_2 + H_2$

20 Reactions I and II produce hydrocarbon products. Reaction III, referred to as the water-gas shift reaction, does not produce hydrocarbon products. In Reaction I, hydrogen and carbon monoxide are consumed in a molar ratio of hydrogen to carbon monoxide ( $H_2/CO$  consumption ratio) of 2 to produce hydrocarbon products. Therefore, if Reaction I were the only reaction occurring during the Fischer-Tropsch synthesis, the  $H_2/CO$  consumption ratio in the process would be 2. The effect of Reactions II and III, however, is to reduce the  $H_2/CO$  consumption ratio.

25 Early Fischer-Tropsch work involved gasification of coal to form synthesis gas. Synthesis gas produced in this manner is typically lean in hydrogen, often having a molar  $H_2/CO$  ratio of only about 0.6 to 0.7. In this situation, because the synthesis gas includes such a low  $H_2/CO$  ratio, reduction of the  $H_2/CO$  consumption ratio caused by Reactions II and III was not detrimental. Rather, Reaction III was generally considered to be

beneficial because it produced additional hydrogen. Consumption of carbon monoxide in Reaction III was not a problem due to the relative surplus of that component in the system relative to hydrogen.

More recently, there has been significant interest in the use of gaseous hydrocarbon feeds, such as natural gas and petroleum gas, as the feed material for producing synthesis gas. Synthesis gas produced from natural gas tends to be rich in hydrogen and lean in carbon monoxide, with a H<sub>2</sub>/CO ratio that is typically 2 or greater. If only Reaction I were present during the Fischer-Tropsch synthesis, a H<sub>2</sub>/CO ratio of 2 in the synthesis gas would be optimal because it would match the H<sub>2</sub>/CO consumption ratio in Reaction I. Unlike the situation with synthesis gas produced by coal gasification, Reactions II and III are detrimental when operating with such a hydrogen-rich synthesis gas, because Reactions II and III consume disproportionately large quantities of carbon monoxide. Therefore, when operating with a hydrogen-rich synthesis gas, it would generally be desirable to promote Reaction I and suppress Reactions II and III.

Cobalt-based catalysts, which tend to promote Reaction I and suppress Reactions II and III, have been proposed as preferred catalysts for Fischer-Tropsch synthesis when operating with a hydrogen-rich synthesis gas. With cobalt-based catalysts, H<sub>2</sub>/CO consumption ratios that approach 2 are readily achievable. One problem with cobalt-based catalysts, however, is that they are expensive. Another problem with cobalt catalysts is that during the Fischer-Tropsch synthesis they tend to produce substantial amounts of undesirable methane and other light hydrocarbons, as opposed to more desirable higher molecular weight hydrocarbon products.

Iron-based catalysts have also been proposed for use in Fischer-Tropsch processes operating with a hydrogen-rich synthesis gas. Iron catalysts are typically substantially less expensive than cobalt catalysts. Also, iron catalysts tend to promote production of the more desirable higher molecular weight hydrocarbon products. A significant problem with iron-based catalysts, however, is that they tend to operate at a low H<sub>2</sub>/CO consumption ratio, due to the higher activity of iron catalysts for promoting Reactions II and III. Consumption ratios of less than 1.2 are typical. The result is that significant carbon in the system is lost as a carbon dioxide waste product, and there is a significant excess of unreacted hydrogen, which is also wasted. This requires additional methane

and oxygen for synthesis gas generation to produce a given quantity of hydrocarbon products. The low H<sub>2</sub>/CO consumption ratio has largely discouraged the use of iron-based catalysts in Fischer-Tropsch operations using hydrogen-rich feed, such as natural gas, to produce the synthesis gas.

5 Accordingly, there is a need for an improved Fischer-Tropsch process in which the inherent advantages of iron-containing catalysts for promoting higher molecular weight products can be realized without the excessive waste of carbon and hydrogen, especially when using a hydrogen-rich synthesis gas, such as is produced from a natural gas feed.

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#### SUMMARY OF THE INVENTION

The present invention provides a Fischer-Tropsch method of hydrocarbon synthesis that permits much higher H<sub>2</sub>/CO consumption ratios to be attained when using iron catalysts and that avoids excessive losses of carbon to waste products. The method of the present invention is, therefore, very desirable when processing a hydrogen-rich 15 synthesis gas, such as may be produced from natural gas or other gaseous hydrocarbon feeds. In one aspect, the method of the present invention involves conducting the Fischer-Tropsch reaction as a staged process with multiple Fischer-Tropsch reactor stages arranged in series and with a very low conversion of carbon monoxide in at least one, and preferably in all, of the Fischer-Tropsch reactor stages. Carbon monoxide conversions 20 are typically less than 70% for each reactor stage, and more preferably in a range of from about 40 to about 60% for each reactor stage. Each Fischer-Tropsch reactor vessel is preferably a slurry reactor, in which particles of the catalyst are in a slurry with high molecular weight hydrocarbon products of the Fischer-Tropsch synthesis.

A significant advantage of the present invention is that it significantly increases 25 the H<sub>2</sub>/CO consumption ratio for iron-based catalysts and, accordingly, also reduces the loss of carbon to the production of carbon dioxide, resulting in a larger quantity of hydrocarbon product from a given quantity of gaseous hydrocarbon feed. With the present invention, it has been found that when the carbon monoxide conversion in a Fischer-Tropsch reactor stage begins to significantly exceed 50%, the water-gas shift reaction 30 (Reaction III) becomes increasingly more active. Therefore, when the carbon monoxide

conversion is maintained at a low level in each reactor stage, the water-gas shift activity may be significantly reduced and it is possible to convert a higher percentage of carbon monoxide in the synthesis gas to hydrocarbon product. The invention requires at least two reactor stages in series, but because the invention involves such a low conversion per reactor stage, it is typically preferred to have at least three reactor stages in series to achieve an acceptable yield of the desired hydrocarbon products.

In a further refinement, the process of the present invention involves intermediate removal of water between Fischer-Tropsch reactor stages, so that the partial pressure of water in the reactor vessels is maintained at a relatively low level, further suppressing Reactions II and III and tending to further increase H<sub>2</sub>/CO consumption ratios. The intermediate water removal, in combination with the low carbon monoxide conversion per reactor stage, can result in a significant improvement in the overall H<sub>2</sub>/CO consumption ratio and accompanying reduction in the loss of carbon to carbon dioxide waste product. With the process of the present invention, a H<sub>2</sub>/CO consumption ratio of at least 1.5, and often significantly higher, can typically be attained when using an iron-based catalyst in a slurry reactor.

In one preferred embodiment of the process of the invention, further operational enhancement is available in which the process is controlled so that the H<sub>2</sub>/CO ratio in the synthesis gas feed and the overall H<sub>2</sub>/CO consumption ratio across all of the series of Fischer-Tropsch reactor stages will have approximately the same values, typically within about 0.2 of each other and preferably even closer. This control is typically accomplished by recycling carbon dioxide from the last reactor stage in the series to the synthesis gas production step. Recycling of the carbon dioxide to balance H<sub>2</sub>/CO feed and consumption ratios, in combination with other features of the process of the invention, conserves carbon in the system for ultimate conversion to hydrocarbon product and tends to lower the H<sub>2</sub>/CO feed ratio so that it is approximately equal to the overall H<sub>2</sub>/CO consumption ratio. The result is that the present invention can provide significant operating advantages through increased hydrocarbon product yield and increased energy conversion efficiency. When the process of the invention is operated in this manner, it is typically possible to produce C<sub>5</sub>+ hydrocarbon products that include at least about 90% of the carbon originally contained in the gaseous hydrocarbon feed, and to operate with

a high energy conversion efficiency, so that the C<sub>5</sub>+ hydrocarbon products have a total heating value of at least about 65% of the total heating value of the gaseous hydrocarbon feed.

While the process of the invention may be operated using any Fischer-Tropsch catalyst, the invention is contemplated for use primarily with iron-based catalysts, due to the significant advantages attainable when using iron-based catalysts with the present invention. Furthermore, certain iron-based catalysts are particularly preferred. One preferred iron-based catalyst is a precipitated iron catalyst of a very fine particle size, typically no larger than about 60 microns. Not to be bound by theory, these very fine precipitated iron catalysts are believed to be advantageous over iron catalysts of a larger particle size, because it is believed that larger iron particles tend to trap and effectively immobilize water in interior pore spaces of the particles, which tends to promote Reaction II and consequently lowers the overall H<sub>2</sub>/CO consumption ratio of the reacting synthesis gas. In contrast, it is believed that with the use of the very fine precipitated iron catalysts, less water tends to become trapped in interior pore spaces of the catalyst particles, significantly suppressing Reaction II.

Other preferred iron-based catalysts for use with the process of the invention are a supported iron catalysts, comprised of a thin layer of iron deposited on a support material, such as silica, alumina or carbon. Because the catalytically active iron layer is thin, it is believed to have a low tendency to trap water in interior pore spaces and to thereby suppress Reaction II, in a manner similar to that noted above with respect to the very fine precipitated iron catalysts. A further advantage of using supported iron catalysts, however, is that a larger particle size can be used relative to precipitated iron catalysts. This larger particle size significantly simplifies separation of the catalyst particles from liquid hydrocarbon products produced during the Fischer-Tropsch synthesis.

#### BRIEF DESCRIPTION OF THE DRAWINGS

For a more complete understanding of the present invention, and the further advantages thereof, reference is now made to the following detailed description taken in conjunction with the drawings, in which:

Fig. 1 is a process flow diagram (PFD) showing one embodiment of the Fischer-Tropsch hydrocarbon synthesis process of the present invention, including a synthesis gas generator and three Fischer-Tropsch reactor stages arranged in series;

5 Fig. 2 is a PFD of another embodiment of the Fischer-Tropsch hydrocarbon synthesis process of the present invention, including carbon dioxide recycle to the synthesis gas generator;

Fig. 3 is a PFD showing yet another embodiment of the Fischer-Tropsch hydrocarbon synthesis process of the present invention, including carbon dioxide recycle, hydrocarbon product recovery and catalyst separation and recycle; and

10 Fig. 4 is a PFD showing one embodiment of a product recovery operation for use with the Fischer-Tropsch hydrocarbon synthesis process of the present invention to convert crude synthesis product to distillate products.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In the following description, the present invention is set forth in the context of a 15 staged reaction system oriented towards Fischer-Tropsch synthesis of hydrocarbons from synthesis gas generated from a natural gas or other gaseous hydrocarbon feed. While the process must include at least two Fischer-Tropsch reactor stages, the description herein is made primarily to the use of three Fischer-Tropsch reactor stages, but the same principles apply equally to the use of smaller and larger numbers of stages.

20 Referring to Fig. 1, one embodiment of the Fischer-Tropsch process is shown in which a gaseous hydrocarbon feed 102 and oxygen gas 104 are fed to a synthesis gas generator 106, where synthesis gas 108 comprising hydrogen and carbon monoxide is generated. Although it is possible to add the oxygen gas 104 in the form of air, the use of a gas stream that is enriched in oxygen gas relative to air, such as may be produced by 25 membrane separation of air, is preferred. Use of a gas stream enriched in oxygen gas reduces the need to process the large quantity of nitrogen present in air. The synthesis gas 108 is fed to the first in a series of three Fischer-Tropsch reactors 110 A, B and C. The Fischer-Tropsch reactors 110 A, B and C each have an internal reactor volume, containing a Fischer-Tropsch catalyst, where the Fischer Tropsch reaction occurs to 30 produce Fischer-Tropsch reaction products, including the desired hydrocarbon products.

The Fischer-Tropsch reactors 110 A, B and C, as shown in Fig. 1, are slurry reactors, meaning that catalyst particles are slurried in a liquid of high molecular weight hydrocarbons generated during the Fischer-Tropsch reaction. As synthesis gas passes through the slurry, hydrogen gas and carbon monoxide react to form hydrocarbon products.

The method of the invention is described with reference to the use of a gaseous hydrocarbon feed, such as natural gas, because such feeds are preferred and are particularly advantageous for use with the present invention, but it should be recognized that in its broadest scope the invention is not limited to such feeds. The method could also be advantageously used with other feed materials (such as coal, tars, bitumen, soot, and petroleum coke) from which synthesis gas could be produced. Furthermore, a combination of different types of feed could be used.

Each of the Fischer-Tropsch reactors 110 A, B and C shown in Fig. 1 represent a different Fischer-Tropsch reactor stage of the staged Fischer-Tropsch reaction. It should be recognized that each Fischer-Tropsch reactor stage could include one or more than one reactor vessel. When a stage includes more than one reactor vessel, the reactor vessels within the stage would be arranged in parallel, with each processing a different portion of feed to that stage. In the case of multiple reactor vessels in a stage, the total reactor volume for the stage would be the sum of the internal reactor volumes of all of the reactor vessels in the stage.

It should be noted that, as used herein, the term "Fischer-Tropsch reaction" does not refer to a single reaction, but to all reactions in a complex reaction system occurring in the reactors 110 A, B and C. In addition, it should be noted that the term "Fischer-Tropsch reaction products" includes all compounds resulting from the Fischer-Tropsch reaction taking place in the reactors 110 A, B and C. Fischer-Tropsch reaction products include, for example, hydrocarbon products, water and carbon dioxide. Furthermore, the "hydrocarbon products" referred to herein may include some quantities of oxygenated hydrocarbons, e.g., alcohols, ketones, aldehydes, etc. These oxygenated components, however, typically comprise only a small portion of the total hydrocarbon products, and preferably less than about 10 weight percent of the total hydrocarbon products.

Exiting each Fischer-Tropsch reactor 110 A, B and C are a gaseous effluent 112 A, B and C and a liquid effluent 114 A, B and C. Each of the liquid effluents 114 A, B and C includes heavier hydrocarbons, such as those of about C<sub>11</sub> and larger. Typically, a large portion of the each of the liquid effluents 114 A, B and C will be in the wax range.

5 Each of the gaseous effluents 112 A, B and C includes lighter hydrocarbons, carbon dioxide, water and unconverted hydrogen and carbon monoxide. Each of the gaseous effluents 112 A, B and C is cooled and then is sent to a separator 116 A, B and C where condensed liquids 118 A, B and C are removed. Noncondensable gases 120 A and B from the first two reactors 110 A and B are fed to the next succeeding reactor in series,

10 10 where unconverted hydrogen and carbon monoxide are reacted to form additional hydrocarbon products. The condensed liquids 118 A, B and C generally include water and liquid hydrocarbons, which are typically in a range of about C<sub>4</sub> to C<sub>11</sub>. Because liquid hydrocarbons are a valuable product, they typically would be further separated from the water and recovered. The noncondensable gases 120 A, B and C generally include carbon

15 15 dioxide, light hydrocarbons (typically about C<sub>4</sub> and smaller) and unconverted hydrogen and carbon monoxide.

As shown in Fig. 1, the noncondensable gases 120 A from the first Fischer-Tropsch reactor 110 A in series are fed to the second Fischer-Tropsch reactor 110 B in series. The noncondensable gases 120 B from the second Fischer-Tropsch reactor 110 B in series are fed to the third Fischer-Tropsch reactor 110 C in series. Accordingly, except for the last reactor in series, the unconverted hydrogen and carbon monoxide from each previous Fischer-Tropsch reactor is sent to the next succeeding Fischer-Tropsch reactor in the series.

An important aspect of the present invention is operation of the process with a low carbon monoxide conversion to Fischer-Tropsch reaction products in at least one, 25 preferably two, and more preferably all three of the Fischer-Tropsch reactors 110 A, B and C. As used herein, the term "carbon monoxide conversion" means the molar percentage of carbon monoxide that reacts to form Fischer-Tropsch reaction products. The carbon monoxide conversion in a single reactor may be determined by comparing the 30 quantity of carbon monoxide fed to the reactor with the quantity of carbon monoxide exiting the reactor, the difference representing the quantity of carbon monoxide